

PATENT SPECIFICATION

NO DRAWINGS

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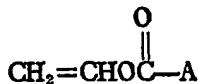
COMPLETE SPECIFICATION

Vinyl N-Heterocyclic Carbamates, Process for their Production
and Polymers thereof

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, 5 State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the 10 following statement:—

This invention relates to new compounds and to methods of making the same. More particularly, this invention relates to vinyl N-heterocyclic carbamates, methods for making vinyl N-heterocyclic carbamates and to polymers of vinyl N-heterocyclic carbamates. 15

The present invention provides new and useful compounds having the general formula



20 in which—A is the residue obtainable by removing the hydrogen atom from a secondary amine group in the ring of an N-heterocyclic secondary amine.

These compounds can be made according 25 to the invention by reacting a vinyl haloformate with an N-heterocyclic secondary amine. In the reaction, the N-heterocyclic secondary amine selected is determined by the structure of the vinyl N-heterocyclic carbamate desired.

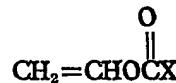
30 The halogen in the vinyl haloformate is preferably chlorine, bromine or iodine. The vinyl haloformate is conveniently vinyl chloroformate. An excess, on a molar basis, of the N-heterocyclic secondary amine over the vinyl haloformate reactant is usually used in the reaction. A molar ratio of 1.5 or more, e.g.,

1.8:1, of N-heterocyclic secondary amine to vinyl haloformate in the starting material is advantageous. The reaction is preferably carried out at below room temperatures, i.e., at a temperature of 10° C. or lower, beneficially at a temperature between -5° and -25° C., for example, -10° C. The products are stable on storage without an inhibitor and on distillation under vacuum.

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As indicated above, the new compounds of this invention are made by reacting a vinyl haloformate having the formula



in which X is a halogen such as chlorine, bromine or iodine with an N-heterocyclic secondary amine having the formula as defined above. Representative specific examples of such N-heterocyclic secondary amines are piperidine, pyrrole, 2-pyrroline, 3-pyrroline, pyrrolidine, ethylene imine (also named aziridine) 3-pyrolidinone, pyrazole, 1,2,3-triazole, 1,2,4-triazole, indole, indoline, carbazole, morpholine, 3-hydro-1,2,3-oxathiazole, purine, hexamethylene imine, piperazine and tetrazole.

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The vinyl N-heterocyclic carbamates of this invention have a pleasant odor and can be employed as odoriferous ingredients in deodorizers. In addition, the compounds of this invention exhibit herbicidal activity. For example, at a concentration of 50 pounds per acre/56 kg/ha, they kill weeds and crabgrass seedlings. The compounds of this invention can also be polymerized to form moldable polymers as will appear hereinafter.

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According to the present invention, the vinyl N-heterocyclic carbamates of this inven-

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[Price 4s. 6d.]

tion can be polymerized to form polymers which can be molded into useful articles such as blocks, sheets and films by conventional techniques. The polymer can be a homopolymer of a vinyl N-heterocyclic carbamate or a copolymer of mixtures of vinyl N-heterocyclic carbamates, or a copolymer of a mixture of one more vinyl N-heterocyclic carbamates with one or more ethylenically unsaturated monomers copolymerizable therewith. Typical monomers copolymerizable with vinyl N-heterocyclic carbamates are styrene and monomers copolymerizable with styrene. Representative examples of such ethylenically unsaturated compounds are the vinyl esters such as vinyl acetate and vinyl butyrate; vinylidene compounds such as vinylidene chloride acrylic and methacrylic acids, acrylates and methacrylates such as ethyl acrylate and methyl methacrylate; acrylonitrile, styrene and substituted styrenes; acrylamides such as N-isopropyl acrylamide; fumaramides; fumaramates; citraconamides; citraconamates; maleamates; maleamides; ethylene; propylene and 1-butene.

Throughout this specification, parts and percentages are parts and percentages by weight unless otherwise specified. The following Examples illustrate the present invention.

EXAMPLE I

In a vessel 43 grams of piperidine are dissolved in 50 milliliters of methylene chloride. There is then added to the solution, with stirring, 26.6 grams of vinyl chloroformate. The temperature of the contents of the vessel is maintained at -10° C. After washing with dilute hydrochloric acid (2 milliliters of HCl in 50 milliliters of water), the mixture is dried by adding 5 grams of anhydrous sodium sulfate and is filtered. Vinyl N-piperidinyl carbamate (24 grams) is then recovered from the filtrate by distillation. It has a boiling point of 68° to 71° C. at 0.35 mm. Hg; $d_4^{25}=1.736$ and $N_D^{25}=1.4768$.

EXAMPLE II

Fourteen grams of pyrrol are mixed with 21.6 grams of vinyl chloroformate and 20 grams of triethylamine (as an HCl acceptor) in 50 milliliters of methylene chloride. Vinyl N-pyrrolyl carbamate (10.5 grams) is separated from the reaction mixture by distillation at a temperature of 78° C. and a pressure of 30 mm. Hg. The product is purified by careful redistillation to yield a colorless liquid. In manner similar to the foregoing Examples, any of the vinyl haloformates indicated above can be reacted with other N-heterocyclic secondary amines as referred to hereinabove to produce vinyl N-heterocyclic carbamates. The products have similar properties and utilities, for example, they can be polymerized as indicated below.

EXAMPLE III

Four grams of vinyl N-piperidinyl carbamate is placed in a glass tube with 0.02 grams of α,α' -azobis(isobutyronitrile) as a catalyst. The tube is sealed under nitrogen. Polymerization takes place at 60° to 61° C. for two days. The viscous product is devolatilized and a solid, moldable resin is recovered.

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EXAMPLE IV

Into a glass test tube is placed four grams of vinyl N-pyrrolyl carbamate along with 0.02 gram of α,α' -azobis(isobutyronitrile). The tube is then sealed in an atmosphere of nitrogen. The tube and its contents are maintained at a temperature of 60° C. for two days. A viscous product results from which the volatile material is then removed leaving a solid resin which is moldable into films, fibers and the like by conventional techniques.

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EXAMPLE V

Into a reaction vessel were placed 11.7 g of vinylchloroformate, 5.2 g. of ethylenimine and 12.1 g. of triethanolamine (as an HCl acceptor) in 50 ml. diethylbenzene containing 0.2 g. of N,N'-diphenylphenediamine. After 83 minutes at 25° C. vinyl N-aziridinyl carbamate was recovered in a yield of 100° C. based on vinylchloroformate.

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EXAMPLE VI

Into a reaction vessel equipped with means for temperature control were placed 10 g. of vinyl N-aziridinyl carbamate, 0.10 g. of α,α' -azobisisobutyronitrile and 100 ml. benzene. The temperature was maintained at 80° C. for 50 hrs. Additional catalyst in amounts of 0.10 g. was added after 6 hours, 25 hours and 27 hours respectively. A polymeric product was obtained, which upon drying was an amber colored solid which charred at 250 to 290° C. It had an aziridine content, determined by infrared analysis and titration with pyridine hydrochloride of 50% of the theoretical value of the homopolymer with all the rings intact.

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EXAMPLE VII

Into a reaction vessel as described in Example VI were placed 5 mls. of vinyl-N-aziridinyl carbamate, 0.65 g. of benzoyl peroxide and 95 mls. of benzene. The temperature was maintained at 80° C. for 49 hours. A polymeric product was obtained which upon drying was a light amber powder. Infrared analysis showed this polymer to have a similar structure as the product of Example VI except that only 25% of the rings were intact.

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In a manner similar to Examples III, IV, VI and VIII, the other vinyl N-heterocyclic carbamates of this invention can be polymerized alone or in admixture with other ethylenically unsaturated monomers as hereinabove indicated in the presence of a polymerization-

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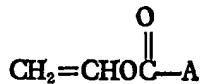
favoring catalyst such as that employed in the Examples or one of the so-called per-catalysts such as the peroxides, for example, hydrogen peroxide and benzoyl peroxide, or such as the persulfates, for example, potassium persulfate to produce solid resins which can be molded into useful shaped articles. Vinyl N-aziridinyl carbamate in particular appears to polymerize through both the aziridine ring and the vinyl group.

WHAT WE CLAIM IS:—

1. A compound having the general formula

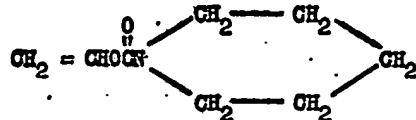
$$\text{CH}_2=\text{CHOC}-\overset{\text{O}}{\parallel}\text{A}$$
- 15 in which—A is the residue obtainable by removing the hydrogen atom from a secondary amine group in the ring of an N-heterocyclic secondary amine.
 2. Vinyl N-piperidinyl carbamate.
 3. Vinyl N-pyrrolyl carbamate.
 4. Vinyl N-aziridinyl carbamate.
- 20 5. A process for preparing a vinyl N-heterocyclic carbamate which comprises reacting a vinyl haloformate with a compound having the general formula HA in which A is the residue obtainable by removing the hydrogen atom from a secondary amine group in the ring of an N-heterocyclic secondary amine.
- 25 6. A process according to claim 5 wherein the vinyl haloformate is vinyl chloroformate.
 7. A process according to claim 5 or claim 6 wherein the compound HA is piperidine.
 8. A process according to any one of Claims 5 to 7 wherein the compound HA is pyrroll.
- 30 9. A process according to any one of Claims 5 to 8 wherein the reaction is carried out at a temperature below 10° C.
- 35 10. A process according to any one of Claims 5 to 9 wherein the reaction is carried out at a temperature between -5° and -25° C.
- 40 11. A polymer of a monomeric material having the general formula

$$\text{CH}_2=\text{CHOC}-\overset{\text{O}}{\parallel}\text{A}$$

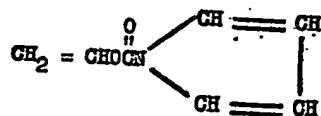


- 45 12. A polymer of a monomeric material having the formula:

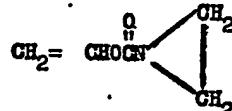
$$\text{CH}_2=\text{CHO}\overset{\text{O}}{\parallel}\text{C}-\text{A}$$



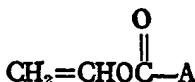
13. A polymer of a monomeric material having the formula:



14. A polymer of a monomeric material 55 having the formula:



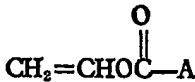
15. A homopolymer of a monomeric material having the general formula:



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in which—A is the residue obtainable by removing the hydrogen atom from a secondary amine group in the ring of an N-heterocyclic secondary amine.

16. A copolymer of a monoethylenically unsaturated polymerizable monomer and a monomeric material having the general formula 65

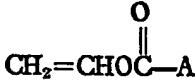


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in which—A is the residue obtainable by removing the hydrogen atom from a secondary amine group in the ring of an N-heterocyclic secondary amine.

17. A process for preparing a vinyl N-heterocyclic carbamate substantially as described in any one of Examples I, II and V. 75

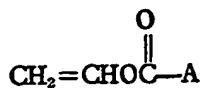
18. A vinyl N-heterocyclic carbamate having the formula



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in which A is as defined in claim 5 whenever prepared by the process claimed in any one of claims 5 to 10 or 17.

19. A polymer of a monomeric material having the formula 85



in which A is as defined in claim 1 substantially as described in any one of Examples III, IV, VI and VII.

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